

Steam reforming of tar derived from the steam pyrolysis of biomass over metal catalyst supported on zeolite



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ABSTRACT

A large amount of tar is generally generated together with synthetic gases (syngas) during steam gasification of biomass, and causes serious problem for the use of the syngas in engines. However, more syngas can be produced if it is reformed by steam during the gasification. In this study, low concentrations of various metal catalysts, i.e., Ni, Fe and Rh, were supported on commercial zeolite beads by incipient wetness impregnation method, and applied for the steam reforming of tar derived from the steam pyrolysis of seaweed in a fixed bed reactor. The effects of metal loading amount and reaction temperature on the tar removal efficiency were investigated in details. It is found that the high hydrogen production yield can be obtained at a reaction temperature above 610 °C even in the case using a low metal loading on zeolite. Among the metal catalysts supported zeolite, Rh showed the most effective for the tar removal and a lower concentration of Rh loaded on zeolite showed a higher catalytic activity, indicating a better dispersion of metal on the surface of zeolite beads. XRD analysis results indicated that metal oxide was reduced to metal during the reaction, suggesting that the reduction gases (H₂ and CO) produced by the steam pyrolysis of biomass and the steam reforming could reduce the oxide to the metal state. Furthermore, these catalysts had an excellent reusability for the reforming of tar derived from steam pyrolysis of seaweed.

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1. Introduction

Today, the increase in energy demand worldwide leads to dramatically depleted fossil fuel resources which causes global warming problem. Therefore, utilization of renewable energy is becoming more and more important. As one of sources of renewable energy, biomass energy refers to any form of plant or animal tissue that contains energy. The production of synthesis gases (syngas) from biomass via gasification is one of the promising thermochemical conversion methods to convert the energy content of biomass into a more practical and clean fuel [1–3]. These gases can be used for synthesis of methanol and liquid fuels by Fischer–Tropsch synthesis, chemical production, and

electricity generation (turbine, gas engine or fuel cell) [4]. However, tar formation is one of the major problems during biomass gasification. Tar is undesirable product and generally generated together with syngas during biomass gasification. It causes a serious problem for the use of the gases in turbines or fuel cells because it is easy to be condensed on cold surfaces and very difficult to be removed [5–7]. Therefore, in a practical process, tar concentration must be controlled at a very low concentration at the exit, and tar elimination is required before further use.

Catalytic steam reforming is the one of potential tar removal techniques from gaseous products by transformation of tar into H₂ and CO in the presence of steam. Catalytic reforming of tar at temperatures in the range of 600–900 °C using various catalysts such as Fe-, Co-, Ni-based catalysts, dolomites, olivine and catalyst-loaded zeolites has been widely studied [8–16]. Zeolite showed good catalytic activities for the catalytic cracking of tar and resulted in a small amount of coke formation on the catalyst [14,17–19]. Dou *et al.* [17] found that Y-zeolite removed almost 100% of tar by catalytic cracking at high-temperature fuel gas when using 1-methylnaphthalene as a model of tar component.

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Transition metal exchanged or impregnated zeolite catalysts were applied for the partial and deep oxidation of hydrocarbons. The results showed that transition metal cations improved the zeolite activity for hydrocarbon conversion by increasing both the zeolite acidity (by cation hydrolysis), and oxygen chemisorption [14]. For instance, addition of copper in Y-zeolites (i.e., CuNaHY zeolite) promoted the oxidation of toluene and accommodated the removal of coke formed in the course of reaction [14].

In order to reduce the cost and improve reforming economics, highly active and stable catalysts are required. In this study, Ni, Fe and Rh with low weight concentrations were supported on commercial zeolite beads, and applied for the steam reforming of tar derived from the steam pyrolysis of seaweeds in a fixed bed reactor at relatively low reforming temperatures. The effects of metal loading amount and reaction temperature on the tar removal efficiency and the reusability of as-prepared catalysts were investigated. Catalysts before and after used were characterized by XRD and discussed.

2. Experimental

2.1. Materials

In this study, seaweed (*Sargassum horneri* (Turner) C. Agardh, Aomori, Japan) was chosen as the biomass sample. It was washed in fresh water and dried in oven at 105 °C for 3 days before storage and further use. The elements of C, H, N, S, and O were analyzed using Elemental Analyzer Vario EL cube (DKSH Japan Co., Ltd.) and it is found that 39.2 wt% C, 5.0 wt% H, 1.9 wt% N, 1.5 wt% S and 52.4 wt% O (diff.) were contained in the dried seaweed. The ash content of this biomass after calcination at 650 °C for 2 h in air was approximately 21.3 wt% based on as received material and its main composition was 54.7 wt% CaO, 16.9 wt% SO₃, 10.3 wt% K₂O, 8.1 wt% P₂O₅, 4.9 wt% SiO₂, 3.6 wt% SrO, 0.9 wt% Fe₂O₃, 0.26 wt% MnO₂, 0.18 wt% Br, 0.1 wt% ZnO and 0.02 wt% As₂O₃ according to XRF analysis (Energy Dispersive X-Ray Spectrometer, EDX-800HS, Shimadzu). Iron (III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O) and rhodium (III) nitrate (Rh(NO₃)₃) were purchased from Sigma-Aldrich Japan Co., Ltd. (Tokyo, Japan). Nickel (II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O) was purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Zeolite F-9 beads with an average diameter of 4 mm was purchased from Tosoh Corporation (Tokyo, Japan).

2.2. Catalyst preparation

Rhodium (Rh), iron (Fe) and nickel (Ni)/zeolite catalysts were prepared by incipient wetness impregnation method using the aqueous solutions of Rh(NO₃)₃, Fe(NO₃)₃·9H₂O and Ni(NO₃)₂·6H₂O, respectively, leading to different metal weight concentrations (0.5–1.5 wt%). After evaporation of the excess of water, the samples were dried overnight at 105 °C and calcined in air at 650 °C for 3 h before storage and further use. The morphology of the metal-loaded zeolite catalysts were characterized with a scanning electron microscope (SEM, S-800, Hitachi, Japan), and structural and compositional analyses before and after reaction were carried out with X-ray diffraction (XRD, Shimadzu, Japan).

2.3. Catalytic activity tests

In a practical process, it is expected to use waste steam from factory to steam reforming of biomass, and in this case, the tar is generally produced due to the steam pyrolysis of biomass. In order to investigate the catalytic reforming of tar derived from the steam pyrolysis of biomass, in this study, experiments were carried out using a fixed-bed reactor with an internal diameter of 18 mm and a

length of 350 mm as illustrated in Fig. 1. For a non-catalytic run, 0.6 g of biomass was loaded into the vertical fixed-bed reactor. For catalytic run, 0.6 g of biomass and 4 g of catalyst were separately loaded into reactor with quartz wool and in this case, the tar derived from the steam pyrolysis of biomass was moved to the catalyst layer with the carrier gas and reformed there. For each run, the heater was started at room temperature with a heating rate of 20 °C/min and held at the desired temperature for 2 h. The reactions were performed at 510, 610 and 660 °C and atmospheric pressure. Argon as a carrier gas with a saturated steam ($p_{\text{H}_2\text{O}} = 70 \text{ kPa}$) flowed down from the top to the bottom of the reactor with a flow rate of 50 ml/min. The gases produced were passed through a cold trap and analyzed every 8 min using an online gas chromatograph (Agilent 7890A GC system), in which one TCD with 3 packed columns (1 molecular sieve 5A column + 1 HayeSep Q column + 1 molecular sieve 5A column) was for the separation of CO, CH₄ and CO₂ using He as carrier gas while the other TCD with a molecular sieve 5A for H₂ measurement using Ar as the carrier gas.

3. Results and discussion

3.1. Steam reforming of the tar derived from the steam pyrolysis of seaweed over different catalysts

The composition of gas product during gasification of biomass is generally affected by properties of catalysts and reaction conditions [20]. In this study, the steam pyrolysis of biomass and the steam reforming of the tar derived from the seaweed were carried out in the fixed bed reactor at reaction temperature of 610 °C with the presence of saturated steam for non-catalytic and catalytic system at first. In catalytic system, 0.5 wt% of Rh, Ni or Fe supported on zeolite beads were used as the catalyst. The structures of these catalysts were characterized by SEM and the results showed in Fig. 2. It is found that different microstructure was observed for different kinds of metal-loaded catalyst and the catalysts were homogeneously dispersed on the surface of the zeolite beads. Especially, macropore structure was formed on the surface of zeolite beads for Fe-loaded catalyst, and velvet-like structure was observed for Ni-loaded catalyst. Fig. 3 compares the gas production yields when different catalysts were used. The major gas components for the produced gases were composed of hydrogen and carbon dioxide and only a small amount of carbon monoxide and methane were detected. In the present reaction system, the steam was introduced in order to proceed to the steam reforming of tar and the water-gas shift (WGS) reactions

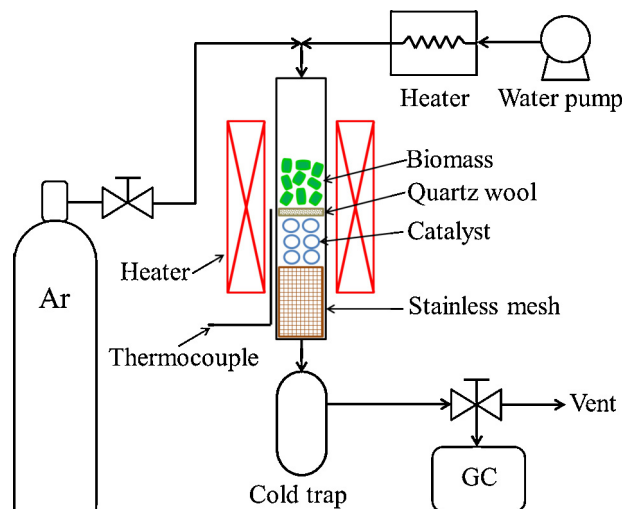


Fig. 1. Schematic diagram of the experiment system.

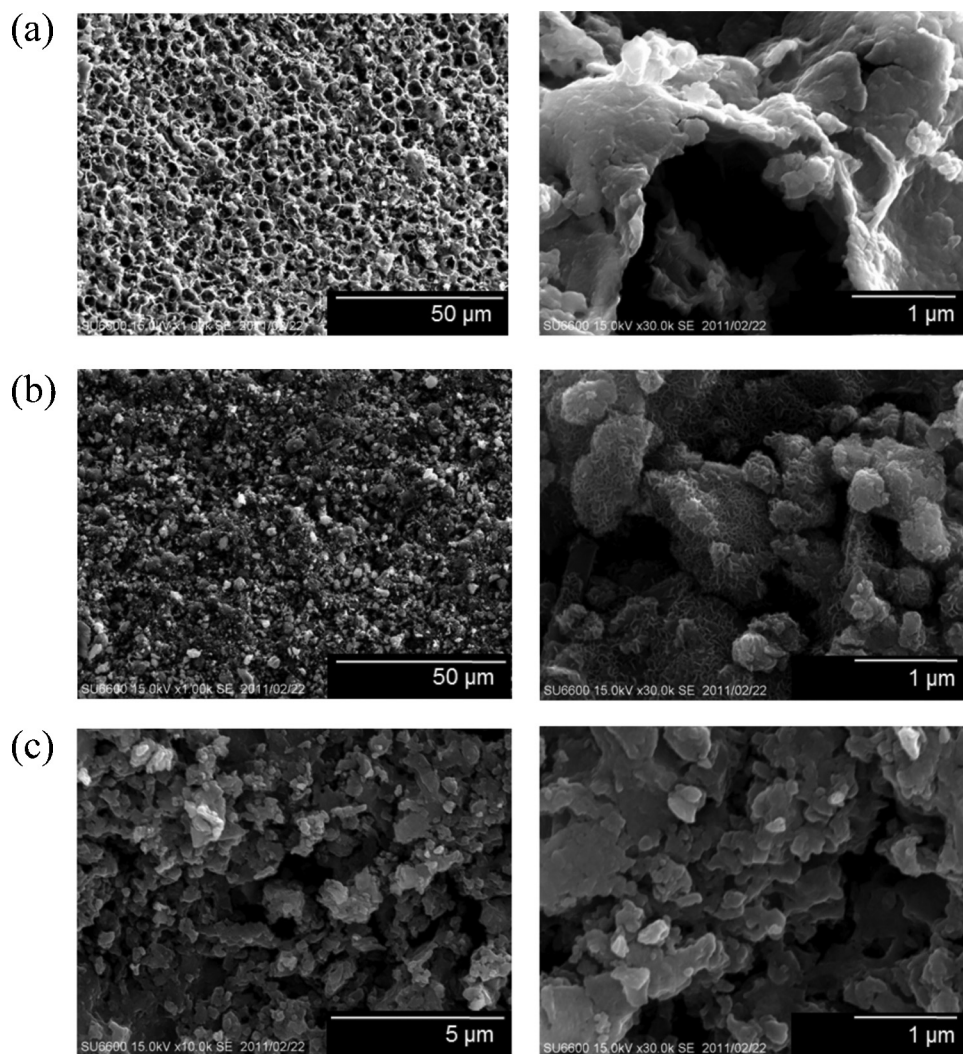


Fig. 2. SEM images of catalysts (a) 0.5 wt% Fe (b) 0.5 wt% Ni and (c) 0.5 wt% Rh.

($\text{H}_2\text{O} + \text{CO} \rightarrow \text{CO}_2 + \text{H}_2$). The presence of steam in the reaction system was expected to facilitate the tar reforming to syngas. The higher amounts of CO_2 and H_2 found in this study indicated that water gas shift reaction should be occurred under the present experimental conditions. It should be noted that the highest gas yield was obtained when 0.5 wt% Rh/zeolite catalyst was used. This result is agreement with those reported in the literature [21]. Compared with the results without catalyst, much higher gas yields were obtained in the present study. It should be noted that in the case of non-catalytic system, hydrogen yield also reached approximately 20 mmol/g-carbon. It might be caused by the self-catalytic activities of some components in biomass such as alkali, alkaline earth species and Fe_2O_3 for the *in situ* steam reforming of tar in the biomass.

3.2. Effects of reaction temperature

Fig. 4 shows the effects of reaction temperature on the catalytic activity of metal-loaded zeolite catalysts for the steam reforming of tar were examined over the range of 510–660 °C. In this study, 0.5 wt% Rh, Ni or Fe supported on zeolite beads was used as the catalyst. As shown in Fig. 4, the reaction temperature had a great effect on the H_2 production yields for all systems. Especially, H_2 production yield increased sharply when the reaction temperature was increased from 510 to 610 °C, but when the reaction temperature was over 610 °C, the increase extent for H_2 production

yield was not so obviously, suggesting that the catalytic activity reached its highest level. If the reaction temperature increased more, catalysts particles dispersed on the surface of the zeolite beads could be sintered and decreased its activity. Many

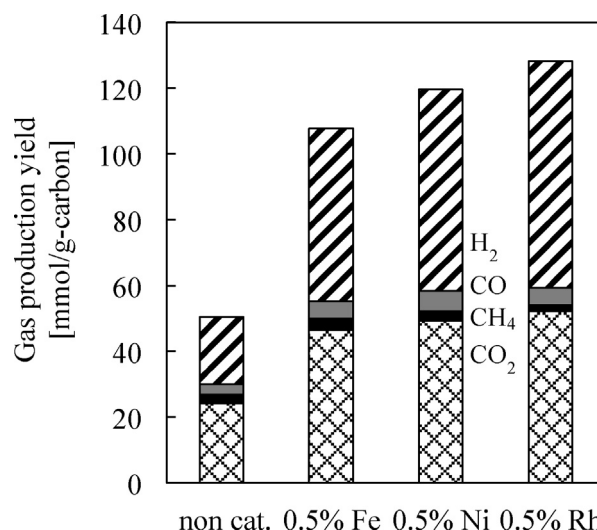


Fig. 3. Gas production yield at a reaction temperature of 610 °C for 2 h.

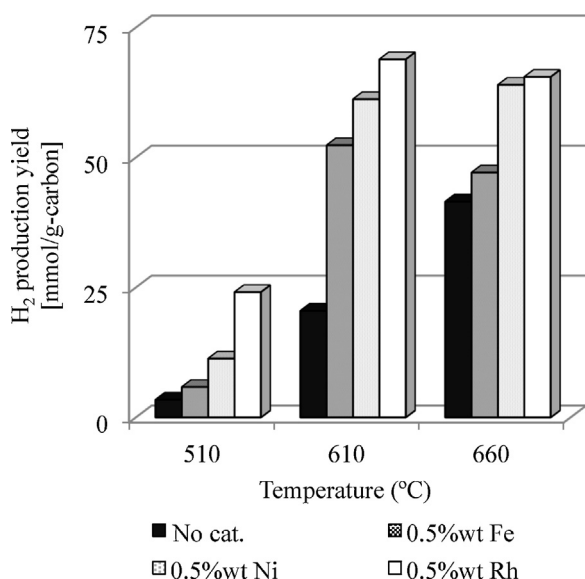


Fig. 4. Effect of reaction temperature on H₂ production yield.

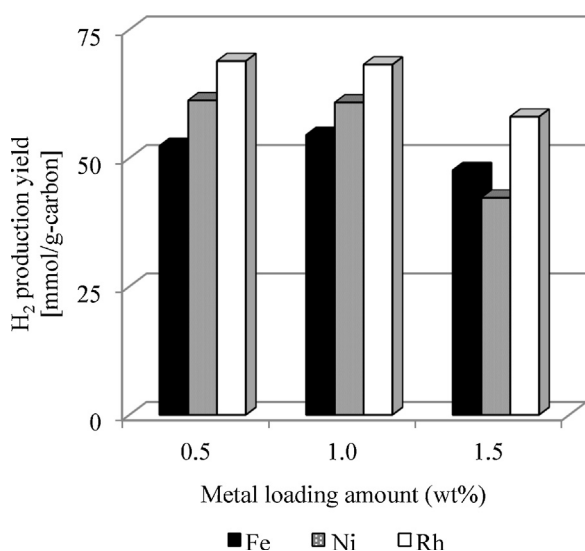


Fig. 5. Effect of metal loading amount on H₂ production yield.

researchers have reported that higher temperatures contributed to higher syngas yield. Increased temperature provides the energy for endothermic reforming reaction of tar and/or char, thereby enhancing the yield of syngas [22–25]. Therefore, in order to achieve a high carbon conversion of the biomass and low tar content in the produced gas, a high operating temperature (above 800 °C) in gasifier is preferred [20]. However, in the present study, a good catalytic activity was also found for the low weight concentration of Rh, Fe or Ni-loaded zeolite catalysts even when the reaction was operated at a temperature as low as 610 °C.

3.3. Effects of metal loading amount

Effects of metal loading amount on the tar removal efficiency were investigated by adjusting the metal loading weight concentration in the range of 0.5–1.5 wt%. Fig. 5 shows the H₂ production yields at the reaction temperature of 610 °C when using catalysts with different metal loading amount on zeolite beads. It is found that a higher H₂ production yields was obtained at lower metal loading for all catalysts. In general, the metal catalyst should be dispersed on the surface of zeolite with a smaller particle size in order to get more active sites. In this study, with the increase in the loading amount, the sintering of metal particle during calcination could occur, resulting in the decrease of the catalytically active sites. Therefore, a lower metal loading amount was found to be suitable for the steam reforming of tar in the present study.

Fig. 6 shows the XRD spectra of 1.5 wt% Rh and Ni-loaded catalyst before and after the reaction. It is found that small peaks of metallic Rh and Ni appeared after the reaction. It indicates that a part or all of the oxides could be converted to metallic iron due to the existence of some reduction gases such as H₂ and CO during the reaction. In our previous study, a similar phenomenon was also observed [26]. It should be noted that the intensities of the major peaks (zeolite) decreased significantly. It is possible that the tar adsorbed on the catalysts still remained on the catalysts or carbon deposited on the catalyst after 2 h reaction.

3.4. Reusability of metal supported zeolite catalysts

High catalytic activity and stable catalyst reusability are important for steam reforming of tar. In this study, the reusability of the catalyst was examined by repeatedly re-using the same catalyst in experiment after regenerated at 650 °C for 3 h in air. As shown in Fig. 7, H₂ production yields decreased slightly in the second run and remained almost constant in the third run for

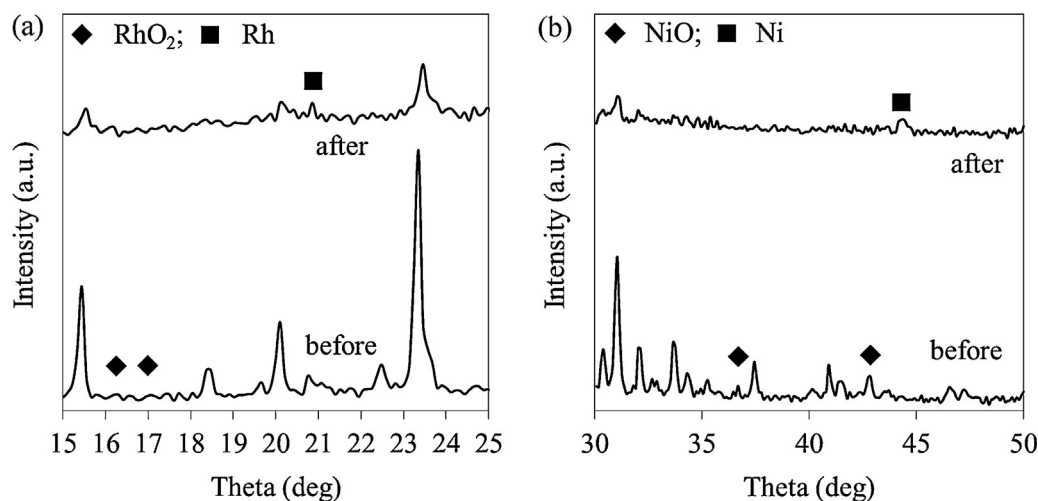


Fig. 6. XRD patterns of catalysts before and after reaction: (a) 1.5 wt% Rh and (b) 1.5 wt% Ni.

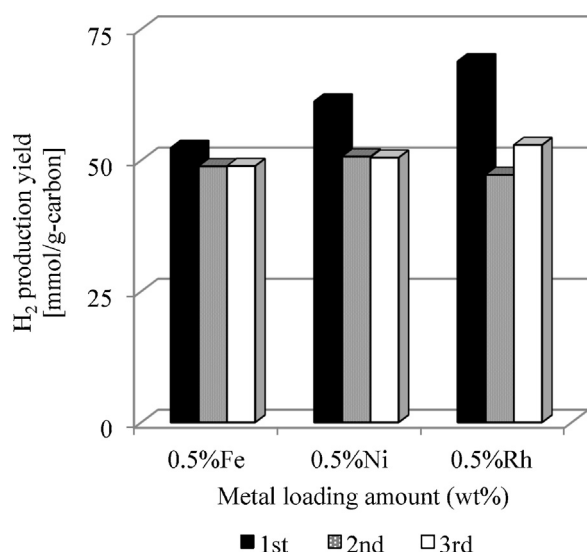


Fig. 7. Reusability of the metal loaded zeolite catalysts for the steam reforming of the tar derived from the steam pyrolysis of seaweed.

Fe- and Ni-loaded zeolite catalyst. As stated in the experimental section, a large amount of sulfur, which could move to the catalyst layer with the tar and poison the active sites, was contained in the seaweed. It might deactivate the catalytic activity even the used catalyst was calcined. On the other hand, the cracking of large sized and thermally unstable constitutive molecules such as carbohydrates, furans and phenols that usually contained in the biomass-derived tar could lead to carbon deposition on the catalyst surface, and reduce catalytic activities. These should be the main reasons why the hydrogen yield decreased to some extent after the first run for all metal supported zeolite catalysts. However, it should be also noted that a part of alkali and alkaline earth metallic species such as potassium could be moved from the biomass with tar and deposited on the catalyst and resulting in the promotion of the catalytic activity to some extent [26]. This should be the main reason to let the catalyst activity remain almost constant run for Fe- and Ni-loaded zeolite catalyst and even increase the catalyst activity for Rh-loaded catalyst in the third run.

4. Conclusions

Catalytic steam reforming of the tar derived from the steam pyrolysis of seaweed was carried out in the fixed bed reactor under atmospheric pressure. Various metals (Ni, Fe and Rh) with low weight concentrations were supported on commercial zeolite beads and their catalytic activities were evaluated at different reaction temperatures. Metal loading amount and reaction temperature were found to have great influence on the steam reforming of tar. High H₂ production yield was obtained at a reaction temperature near 610 °C even with a low metal loading amount. Rh-loaded catalysts showed the highest tar reforming efficiency among the examined catalysts. These catalysts had an excellent reusability for the reforming of tar derived from the steam pyrolysis of seaweed.

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